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16. ABSTRACT

A technique is presented for finding the least squares estimates for the ultimate biochemical oxygen demand (BOD) and rate coefficient for the BOD reaction without resorting to complicated computer algorithms or subjective graphical methods. The technique can easily be implemented on advanced programmable calculators or mini-computers and is effective if the BOD time series reasonably follows the first-order model and the nitrification stage has been suppressed

This may be used in stream water quality surveys and operational studies of sewage treatment plants.

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PROPOSED MODIFICATIONS OF K_2-TEMPERATURE RELATION

By Linfield C. Brown[1] and Michael K. Stenstrom,[2] A. M. ASCE

INTRODUCTION

The technical note by Howe (5) serves as a good example of the pitfalls associated with an inadequate analysis of aeration data. Howe (5) presents experimental data from two unsteady aeration tests (see Table 1). These data are used to show that the reaeration coefficient varies inversely with temperature. This finding is counter to the accepted temperature dependence of K_2. It is well recognized in the literature that oxygen transfer coefficients increase with increasing temperature, other factors remaining constant (2).

The writers believe that Howe's (5) conclusion is unfounded and that it is the result of an inadequate statistical analysis of data from poorly designed experiments. The analysis suffers from at least three deficiencies: (1) An inappropriate method for determining the value of the mass transfer coefficient, K_2; (2) a lack of data taken during the unsteady aeration tests; and (3) an oversight in not computing the precision of the estimated values of K_2. An explanation of these deficiencies and a reanalysis of the data follows.

COMPARISON OF DATA ANALYSIS TECHNIQUES

A variety of graphical and numerical procedures have been proposed for the analysis of unsteady-state oxygen transfer data. A general review of these procedures has been given by Brown (4). They are conveniently grouped into three categories, i.e., the exponential, log deficit, and direct methods, and they will be summarized herein. The methods derive their name from the form of the equation used to fit the data. The basic oxygen transfer model can be expressed in three forms; first the direct or differential form:

$$\frac{dC_t}{dt} = K_2(C_s - C_t) \quad \ldots \quad (1)$$

Second, the log deficit form:

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$$\ln (C_s - C_t) = \ln (C_s - C_o) - K_2 t \quad (2)$$

And third, the exponential form:

$$C_t = C_s - (C_s - C_o) \exp(-K_2 t) \quad (3)$$

in which C_t = the dissolved oxygen concentration at time t; K_2 = the reaeration (oxygen transfer) coefficient; C_s = the equilibrium (steady-state) dissolved oxygen concentration; and C_o = the dissolved oxygen concentration at time zero. The notation used in Eqs. 1, 2, and 3 is consistent with that of Howe (5).

The exponential form of the oxygen transfer model, Eq. 3, is best suited for the analysis of unsteady-state oxygen transfer data (3,6). It requires a nonlinear least squares regression technique to estimate the values of C_o, C_s, and K_2, but has the following advantages. It provides the least squares estimates and precision of these estimates for all three parameters directly from the data; it works directly with the observed dissolved oxygen concentration, C_t, rather than with a calculated log dissolved oxygen deficit, or with an approximation

TABLE 1.—Comparison of Parameter Estimates

Parameter (1)	Set I—20.5C		Set II—30C	
	Howe's data[a] (2)	Writer's data[b] (3)	Howe's data[a] (4)	Writer's data[b] (5)
K_2, per hour	1.221	1.016 ± 18%	1.085	1.011 ± 2.9%
C_s, in milligrams per liter	9.75	10.36 ± 6.4%	7.75[c]	7.81 ± 0.7%
C_o, in milligrams per liter	0.00[c]	−0.048 ± 0.45	0.00[c]	0.004 ± 0.06

[a]Howe's method—log deficit.
[b]Writer's method—exponential.
[c]Assumed value.

to the time rate of change of oxygen concentration; it does not require the truncation of observed data as the dissolved oxygen concentration approaches saturation; and it provides parameter estimates that are more precise than those given by other commonly-used methods.

While the nonlinear regression method using Eq. 3 is recommended for parameter estimation, methods employing graphical, or linear least squares numerical techniques, or both, may be useful for obtaining approximate values for the parameters. The log deficit method using a measured value of C_s to compute the deficits has the advantage of being linear in K_2. The disadvantage is that the value of C_s must be assumed, and thus, the estimate of K_2 will be biased to the extent that C_s is selected incorrectly. Furthermore, the method does not yield estimates of the precision of C_s, and often requires truncation of the data in the vicinity of saturation.

The direct method is another useful approximate method and has the advantage of not requiring that C_s be specified in order to estimate K_2. However, the differentiation inherent in the direct method produces a variable dC_t/dt, having

a larger error than the error in C_t. The larger error in dC_t/dt causes the error in the parameter estimates, C_s and K_2, to be larger than those from other methods.

It appears from the data and calculations in Table 1 of Howe's work (5), that he used the log deficit method for estimating the reaeration coefficient. It is not clear how the values of C_s used in the calculations were selected. A value of C_s larger than the best fit value (in a least square sense) will result in a negative bias to the estimated mass transfer coefficient. To avoid this problem, the writers have used the exponential method to fit Eq. 3 to Howe's data. A comparison of the results of the two estimation procedures is given in Table 1.

For data set I (20.5C), the least squares estimate of K_2 by the exponential method is 16% lower than that reported by Howe. Correspondingly, the estimate of C_s is 6% higher than the value assumed by him. For data set II (30C), the least squares estimates of K_2 and C_s by the exponential method are 7% lower and 1% higher, respectively, than the values reported by Howe. Two important observations can be made from this comparison. First, the estimates of K_2 by the two estimation methods differ for both sets of data. Second, using the exponential method, the estimates of K_2 for set I (20.5C) differ from that for set II (30C) by less than 1%.

Another disturbing feature in the analysis is the manner in which Howe uses the zero-zero concentration-time pair. From inspection of his Figs. 1, 2, and 3, and the fitted equations he reports, it appears that Howe forces the equation through the origin. It is the writers' experience in unsteady aeration testing that it is practically impossible to define the precise point in time at which the dissolved oxygen concentration changes from zero to steadily increasing values. Time zero is usually established arbitrarily near the point in a test where the reaeration curve begins to increase. Thus, the value of concentration at time zero should be treated similarly to any other observation, subject to experimental error. Forcing the model through the origin potentially biases the other parameter estimates.

Experimental Design

According to Berthouex and Hunter (1), parameter estimation is most efficient if care is taken in selecting the times at which observations of the dependent variable are made. For models of the type of Eq. 3, it can be shown that the important observation times are zero, $1/K_2$, and times approaching infinity. These times correspond to the maximum sensitivity of C_o, K_2, and C_s, respectively. Thus, an efficient experimental design should reflect these sensitivities. The regression analysis with Eq. 3 therefore should be based on a minimum of 10–15 data values. Approximately two-thirds of these values should be evenly distributed over the time period of $0/K_2$–$2/K_2$ (or approx 0%–86% equilibrium dissolved oxygen concentration). The remaining one-third of the values should be evenly distributed over the time period of $2/K_2$–$4/K_2$ (or 86%–98% equilibrium). If there is considerable uncertainty about the anticipated value of K_2, then the test should be conducted for as long a period of time as possible to insure a length of at least $4/K_2$.

Howe's table 1 shows that only 5 and 6 observations for data sets I and

II, respectively, were used in the analysis. Although the division of data values above and below $2/K_2$ is probably acceptable, clearly there are too few observations in each region for good parameter estimation. Especially important are more data at the beginning of each experiment (the dissolved oxygen range from 0 mg/l–5 mg/l), because the estimate of K_2 is sensitive to values in this region. In addition, data set I was not carried out for a sufficient length of time (for this set $4/K_2$ is about 4 h). It is unfortunate that Howe does not fully report his experimental procedures. For example, it is not reported how the test water was deaerated, or if normally accepted methods were used. Numerous investigators have reported spurious results in determining K_2, which were produced by faulty deaeration techniques. Also, Howe does not indicate how power input was measured to insure that equal power was used for both test temperatures. At the Reynolds number used in these two experiments, small changes in fluid viscosity should not change power input; however this should be confirmed experimentally and not assumed. A small change in power input could produce a change in K_2 much greater than the Howe's proposed temperature effect.

Precision of Parameter Estimates

In addition to the least squares estimates, the standard deviations or relative standard deviations of the parameter estimates should be calculated and reported. The parameter standard deviations reflect the degree of scatter in the data and should be small (say less than 5% of the least squares estimate) for a good experiment. The standard deviations are also useful in comparing the least squares parameter estimates from one experiment to another.

The precision of the parameter estimates by the exponential method for data sets I and II are presented in Table 1 as relative standard deviations. For data set I they are high, 18.6% for K_2 and 6.4% for C_s, while for data set II they are low, 2.9% and 0.7%, respectively. The reason for the better precision in data set II is probably because the data are less noisy than in set I and because the experiment in set II was carried out for a longer period of time.

A statistical test of the hypothesis comparing the reaeration coefficient from set I (20.5C) with that from set II (30C) shows no significant difference between the parameter estimates from the two sets at a 95% confidence level. Although the estimate of K_2 is lower at 30C than at 20.5C, the difference between the two values is easily attributable to experimental error, rather than to a potential temperature effect.

Summary

The precise estimation of reaeration coefficients from unsteady-state oxygen transfer data is not a trivial exercise. It requires an unambiguous estimation technique and an adequate set of observed values of concentration versus time. In addition, many unsteady aeration tests performed over a wide range of temperatures are required to verify a postulated temperature dependence of the reaeration coefficient. The data reported by Howe (5) do not provide any support for a "new theory" of an inverse temperature dependence for the reaeration coefficient.

Appendix.—References

1. Berthouex, P. M., and Hunter, W. G., "Problems Associated with Planning BOD Experiments," *Journal of the Sanitary Engineering Division*, ASCE, Vol. 97, No. SA3, Proc. Paper 8202, June, 1971, pp. 333–334.
2. Bewtra, J. K., Nicholas, W. R., and Polkowski, L. B., "Effect of Temperature on Oxygen Transfer in Water," *Water Research*, Vol. 4, 1980, pp. 115–123.
3. Boyle, W. C., Berthouex, P. M., and Rooney, T. C., "Pitfalls in Parameter Estimation for Oxygen Transfer Data," *Journal of the Environmental Engineering Division*, ASCE, Vol. 100, No. EE2, Proc. Paper 10451, Apr., 1974, pp. 391–408.
4. Brown, L. C., "Oxygen Transfer Parameter Estimation," *Proceedings: Workshop Toward an Oxygen Transfer Standard*, EPA-600/9-78-021, U.S. Environmental Protection Agency, Apr., 1979, pp. 27–40.
5. Howe, R. H. L., "Proposed Modification of K_2-Temperature Relation," *Journal of the Environmental Engineering Division*, ASCE, Vol. 103, No. EE4, Proc. Paper 13098, Aug., 1977, pp. 729–732.
6. Stenstrom, M. K., "Models for Oxygen Transfer: Their Theoretical Basis and Implications for Industrial Wastewater Treatment," *Proceedings*, 33rd Industrial Waste Conference, Purdue Univ., Lafayette, Ind., May, 1978, pp. 679–686.

Least Squares Estimates of BOD Parameters

By Thomas O. Barnwell, Jr.,[1] A. M. ASCE

Introduction

In stream water quality surveys and in operational studies of sewage treatment plants, long-term biochemical oxygen demand (BOD) tests are often conducted. The purpose of these tests is to find the ultimate oxygen demand of a waste and the first-order rate coefficient for the BOD reaction. This information is mandatory if a water quality model is to be used. This paper presents a technique for finding the least squares estimates for the ultimate BOD and rate coefficient without resorting to complicated computer algorithms or subjective graphical methods. The technique can easily be implemented on advanced programmable calculators or mini-computers and is effective if the BOD time series reasonably follows the first-order model and the nitrification stage has been suppressed.

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Background

Several methods are available that give a fair estimate of the ultimate BOD and reaction rate coefficient provided that the observed data fit a first-order reaction. An Environmental Protection Agency (EPA) training manual (11) noted five methods, i.e., the least squares method of Reed and Theriault (7), the Thomas Slope Method (9), the Method of Moments (6), the Rapid Ratio Method (8), and the Daily Difference Method (10). Berthouex and Hunter (2,3) analyzed the BOD test from an optimal experimental design standpoint. They described the least squares method of parameter estimation and applied it to the first-order equation. They pointed out that, in the case of the BOD experiment, the model is nonlinear and that the least squares estimates of the parameters cannot be solved for explicitly. This paper describes a method for implementing their analysis on hand calculators and small computers.

Development of Least Squares Model

The equation describing the oxygen utilized in the BOD test is

$$Y = L\,[1 - \exp(-kt)] \qquad (1)$$

in which t = time; Y = the BOD; L = the ultimate BOD; and k = the reaction rate coefficient. This equation is nonlinear in the parameters and, therefore, the least squares estimates cannot be obtained directly. Draper and Smith (5) describe a procedure for finding least squares estimates in the nonlinear case. In the method of least squares, a quantity called the sum of squares is used to measure how well the calculated and observed results agree. This sum of squares can be written as

$$S = \sum_{i=1}^{n} (Y_{obs,i} - Y_{calc,i})^2 \qquad (2)$$

in which S = the sum of squares; $Y_{obs,i}$ = the ith experimental observation; $Y_{calc,i}$ = the ith value calculated using the experimental model; and n = the total number of experimental observations. The least squares estimates of the model parameters are those values that minimize the sum of squares. In the case of the BOD model, the model parameters are k and L, and the least squares model can be written as

$$S(L,k) = \sum_{i=1}^{n} \{Y_{obs,i} - L\,[1 - \exp(-kt_i)]\}^2 \qquad (3)$$

in which t_i = the time of the ith observation. This equation is formed by substituting Eq. 1 into Eq. 2. At the point where S is the minimum, the partial derivatives of S with respect to each of the parameters must equal zero:

$$\frac{\partial S}{\partial L} = -2\sum_{i=1}^{n} \{Y_{obs,i} - L\,[1 - \exp(-kt_i)]\}(1 - \exp(-kt_i)) = 0 \qquad (4)$$

$$\frac{\partial S}{\partial k} = -2\sum_{i=1}^{n} \{Y_{obs,i} - L\,[1 - \exp(-kt_i)]\}(t_i L \exp(-kt_i)) = 0 \qquad (5)$$

In order to simplify the notation at this point, let $y = Y_{obs,i}$; $x = [1 - \exp(-kt_i)]$; and $z = t_i \exp(-kt_i)$. All summations run from $i = 1$ to n. Using this notation, the two simultaneous Eqs. 4 and 5 can be rearranged and written

$$\Sigma xy - L\Sigma x^2 = 0 \quad \ldots \quad (6)$$

$$\Sigma yz - L\Sigma xz = 0 \quad \ldots \quad (7)$$

Solving the two equations for L gives

$$L = \frac{\Sigma xy}{\Sigma x^2} \quad \ldots \quad (8)$$

$$L = \frac{\Sigma yz}{\Sigma xz} \quad \ldots \quad (9)$$

The value of k, denoted $\hat{k}$, that gives the same value of L in both expressions is the least squares estimate of k, and the corresponding value of L, denoted $\hat{L}$, is the least squares estimate of L. This value cannot be solved for directly, but must be found using an iterative procedure. This is done by first forming a function of k such that

$$f(\hat{k}) = \frac{\Sigma xy}{\Sigma x^2} - \frac{\Sigma yz}{\Sigma xz} = 0 \quad \ldots \quad (10)$$

Newton's method (4) can be used to find the zero of $f(x)$. For the iterative procedure, the expression

$$k_{j+1} = k_j - \frac{f(k_j)}{f'(k_j)} \quad \ldots \quad (11)$$

[in which $f'(k_j)$ = the first derivative of $f(k_j)$ with respect to k] is successively evaluated until a satisfactory estimate of k is found. Using a numerical approximation for the derivative, Eq. 11 becomes

$$k_{j+1} = k_j - f(k_j)\left[\frac{k_j - k_{j-1}}{f(k_j) - f(k_{j-1})}\right] \quad \ldots \quad (12)$$

This method requires an estimate of k to start the iteration. Successive approximations are found until $k_{j+1} - k_j$ is less than some specified error criterion. The technique is easily programmed on a digital computer and has been coded for a programmable hand calculator.

Confidence Regions

Confidence contours are defined by taking $S(L,k)$ to be a constant [Draper and Smith (5)]. In the general nonlinear least squares case, it is not possible to define the exact $100(1 - q)\%$ confidence level associated with a contour. However, an *approximate* $100(1 - q)\%$ confidence contour is given by

$$Sq = S(\hat{L},\hat{k})\left\{1 + \frac{p}{n-p} F(p, n-p, 1-q)\right\} \quad \ldots \quad (13)$$

in which p = the number of model parameters; n = the number of observations; q = the confidence level; and F = the inverse function of an F distribution. The value $S(\hat{L},\hat{k})$ is the minimum sum of squares. Draper and Smith point out that the contour so determined will be a proper, correct confidence contour, only the associated confidence level is approximate.

For the BOD model, in which $p = 2$, the inverse F distribution is

$$F(2, n-2, 1-q) = \frac{n-2}{2}\left[q^{-2/n-2} - 1\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

Thus, the approximate $100(1 - q)\%$ confidence contours for the BOD model are given by

$$Sq = S(\hat{L},\hat{k})[q^{-2/n-2}] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

Given a value of q, the associated values of L and k must be found that correspond

TABLE 1.—Least Squares Fit of BOD Data

Time, in days (1)	Observed BOD, in milligrams per liter (2)	Predicted BOD, in milligrams per liter (3)
1.0	0.6	0.38
2.0	0.7	0.72
4.0	1.5	1.33
6.0	1.9	1.84
8.0	2.1	2.28
10.0	2.6	2.64
12.0	2.9	2.95
14.0	3.7	3.21
16.0	3.5	3.43
18.0	3.7	3.62
20.0	3.8	3.78

Note: Error sum of squares = 0.14314; and prediction equation, $Y = 4.63\ [1 - \exp(-0.084t)]$.

to Sq in the expression

$$Sq = \sum_{i=1}^{n} \{Y_{obs,i} - L\ [-\exp(-kt_i)]\}^2 = S(\hat{L},\hat{k})[q^{-2/n-2}] \quad \ldots\ldots\ldots \quad (16)$$

Using the aforementioned simplifying notation, Eq. 16 can be written as

$$Sq = \Sigma\{y - Lx\}^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (17)$$

in which the summation runs from $i = 1$ to n. Squaring the term in brackets, distributing the summation, and carrying Sq across the equals sign gives

$$L^2\Sigma x^2 - 2L\Sigma xy + \Sigma y^2 - Sq = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (18)$$

which is in the form of the quadratic equation and has roots at

$$L = \frac{\Sigma xy \pm [(\Sigma xy)^2 - \Sigma x^2 (\Sigma y^2 - Sq)]^{1/2}}{\Sigma x^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (19)$$

For a given value of k and q, two values of L can be computed that over a range of values of k, will define the $100(1 - q)\%$ confidence contour.

Example.—The data in Table 1 are for a sample taken from the Holston River below Kingsport, Tenn., during August 1977. Nitrification was suppressed

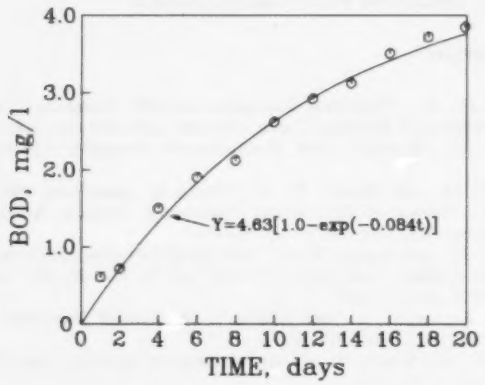

FIG. 1.—Least Squares Fit of BOD Data

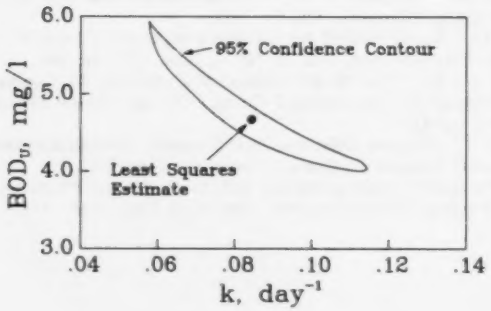

FIG. 2.—Confidence Contour for BOD Data

in the BOD test. A k of 0.15/day was used for the initial estimate. The procedure converged to five decimal places in six iterations. The data and least squares prediction equation are shown in Fig. 1. Most people familiar with this type of test would consider the curve an excellent fit of the data. However, the 95% confidence contour (see Fig. 2), shows the parameter estimates to be highly correlated and imprecise.

Conclusions

A practical technique for least squares estimates of BOD parameters has been developed. The technique is suitable for programmable hand calculators and small computers. The technique has been extended to show how confidence regions for the parameter estimates can be easily determined, and some suggestions for an optimum experimental design are reviewed. The confidence regions could be very useful if, e.g., two analysts arrived at very different estimates for ultimate BOD. Given the hyperbolic shape of the confidence region, very different values for ultimate BOD could lie within it.

Appendix.—References

1. Barnwell, T. O., Jr., "Nonlinear Estimation of BOD Parameters Using Marquart's Compromise Method," Pollution Control Systems and Analysis Activity, Surveillance and Analysis Div., Region 4, U.S. Environmental Protection Agency, Athens, Ga., 1972.
2. Berthouex, P. M., and Hunter, W. G., "Problems Associated with Planning BOD Experiments," *Journal of the Sanitary Engineering Division*, ASCE, Vol. 97, No. SA3, Proc. Paper 8202, June, 1971, pp. 333–344.
3. Berthouex, P. M., and Hunter, W. G., "Statistical Experimental Design: BOD Tests," *Journal of the Sanitary Engineering Division*, ASCE, Vol. 97, No. SA4, Proc. Paper 8286, Aug., 1971, pp. 393–407.
4. Carahan, B., Luther, H. A., and Wilkes, J. O., *Applied Numerical Methods*, John Wiley and Sons, Inc., New York, N.Y., 1969.
5. Draper, N. R., and Smith, H., *Applied Regression Analysis*, John Wiley and Sons, Inc., New York, N.Y., 1966.
6. Moore, E. W., Thomas, H. A., Jr., and Snow, W. B., "Simplified Method for Analysis of BOD Data," *Sewage and Industrial Wastes*, Vol. 22, No. 10, Oct., 1950, pp. 1343.
7. Reed, L. J., and Theriault, E. J., "The Statistical Treatment of Velocity Data," *Journal of Physical Chemistry*, Vol. 35, 1931.
8. Sheehy, J. P., "Rapid Method for Solving First Order Equations," *Journal Water Pollution Control Federation*, Vol. 32, No. 6, June, 1960, pp. 646.
9. Thomas, H. A., Jr., "The 'Slope' Method of Evaluating the Constants of the First Stage Biochemical Oxygen Demand Curve," *Sewage Works Journal*, Vol. 9, No. 3, Mar., 1937, pp. 425.
10. Tsivoglou, E. C., "Oxygen Relationships in Streams," *Technical Report W58-2*, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, 1958.
11. *Water Quality Studies Training Manual*, U.S. Environmental Protection Agency, Office of Water Programs, Training Program, Cincinnati, Ohio, Nov., 1971.